

# Flame Retardants

by Eli M. Pearce<sup>\*†</sup> and R. Liepins<sup>\*</sup>

The four processes involved in the flammability of materials are described and related to the various flame retardance mechanisms that may operate. Following this the four practical approaches used in improving flame retardance of materials are described. Each approach is illustrated with a number of typical examples of flame retardants or synthetic procedures used. This overview of flammability, flame retardance, and flame retardants used is followed by a more detailed examination of most of the plastics manufactured in the United States during 1973, their consumption patterns, and the primary types of flame retardants used in the flame retardance of the most used plastics. The main types of flame retardants are illustrated with a number of typical commercial examples. Statistical data on flame retardant market size, flame retardant growth in plastics, and price ranges of common flame retardants are presented.

## Flammability Process and Flame Retardance

Fundamentally, four processes are involved in polymer flammability (Fig. 1): (1) preheating, (2) decomposition, (3) ignition, and (4) combustion and propagation.

Preheating involves heating of the material by means of an external source which raises the temperature of the material at a rate dependent upon the thermal intensity of the ignition source, thermal conductivity of the material, specific heat of the material, and latent heat of fusion and vaporization of the material.

When sufficiently heated, the material begins to degrade, i.e., it loses its original properties as the weakest bonds begin to break. Gaseous combustion products may be formed with the rate dependent upon such factors as intensity of external heat, temperature required for decomposition, and rate of decomposition.

Flammable gases increase until a concentration is reached that allows sustained oxidation in the presence of the ignition source. The ignition characteristics of the gas and the avail-

ability of oxygen are two important variables in any ignition process. After ignition and removal of the ignition source, combustion becomes self-propagating if sufficient heat is generated and is radiated back to the material to continue the decomposition process. The combustion process is governed by such variables as rate of heat generation, rate of heat transfer to the surface, surface area, and rates of decomposition. Flame retardancy, therefore, can be improved (achieved) by retarding (eliminating) any one of these processes. Figure 2 illustrates how flame retardancy may be improved in the heating stage (1).

Flame retardancy is improved by flame retardants that cause the formation of a surface film of low thermal conductivity and/or high reflectivity that reduces the rate of heating (A). It is also improved by flame retardants that might serve as a heat sink by being preferentially decomposed at a low temperature (B). And finally, it is improved by flame retardant coatings that upon exposure to heat may intumesce into a foamed surface layer with low thermal conductivity properties (C).

Figure 3 illustrates how flame retardancy is improved in the decomposition stage (1). A flame retardant can promote transformation of a plastic into char and thus limit production of combustible carbon-containing gases (A). Simultaneously, the char will decrease thermal

<sup>\*</sup> Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709.

<sup>†</sup> Present address: Chemistry and Chemical Engineering Departments, Polytechnic Institute of New York, Brooklyn, New York 11201.

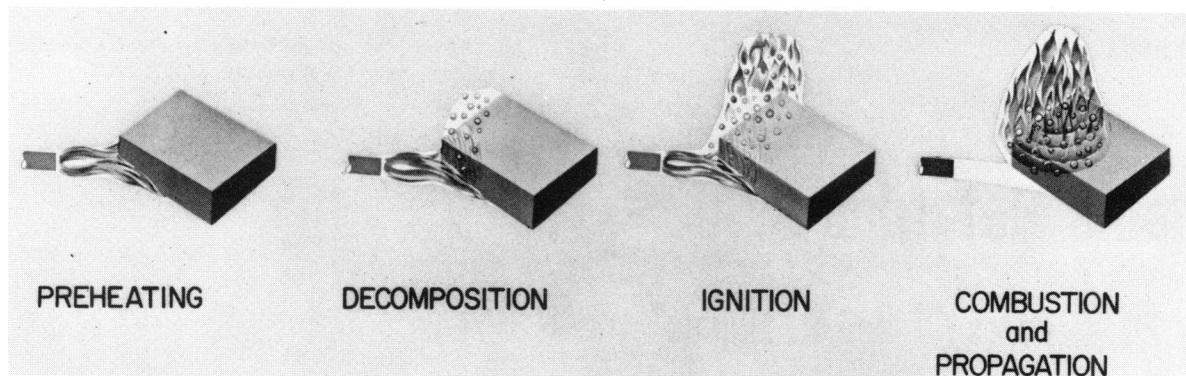


FIGURE 1. Processes involved in polymer flammability.

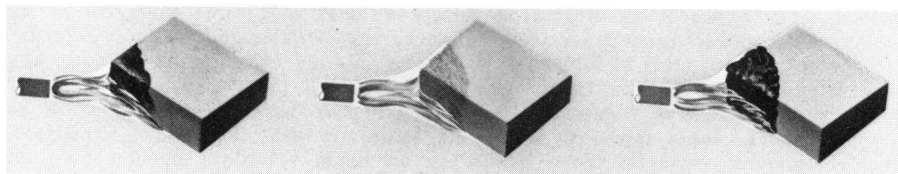


FIGURE 2. Fire retardancy in the preheating stage.

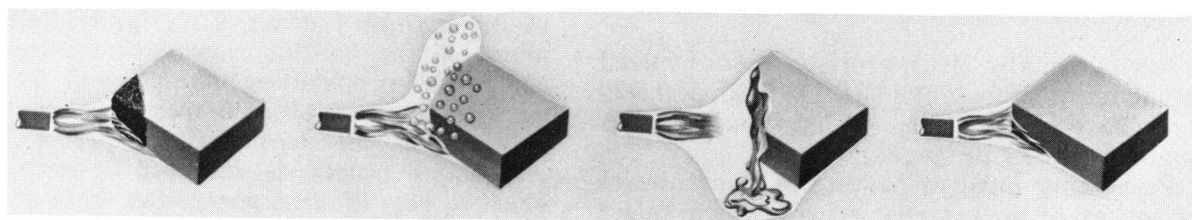


FIGURE 3. Fire retardancy in the decomposition stage.

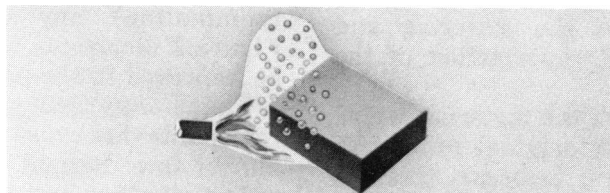


FIGURE 4. Fire retardancy in the ignition stage.

conductivity of the surface. Flame retardants can also chemically alter the decomposition products, resulting in a lower concentration of combustible gases (B). Reduced fuel will thus result in less heat generation by the flame and may lead to self-extinguishment.

Structural modification of the plastic, or use of a flame retardant additive, might induce decomposition or melting upon exposure to a heat source so that the material shrinks or drips

away from the heat source (C). And finally, through selection of chemically stable structural components or structural modifications of a polymer, it is also possible to significantly retard the decomposition process (D).

Figure 4 illustrates flame retardancy in the ignition stage (1). In general, anything that will prevent the formation of a combustible mixture of gases will prevent ignition. In this sense, all of the previously mentioned approaches are

pertinent. However, we may also distinguish those cases in which the flame retardant or the modified polymer unit upon exposure to a heat source will form gas mixtures that will react chemically in the gas phase to inhibit ignition.

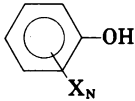
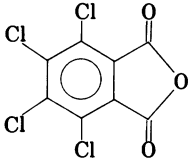
The goal of flame retardance in the combustion and propagation stage is simply to decrease

the rate of heat generated or radiated back to the substrate. Any or all of the above discussed mechanisms could function to prevent a self-sustaining flame.

## Practical Methods of Flame Retardation

Flame retardation is achieved in the follow-

Table 1. Typical flame retardants used as additives.

Class	Example
<b>Nonreactive, organic</b>	
Phosphate esters	$[\text{CH}_3(\text{CH}_2)_7\text{O}]_3\text{—PO}$
Halogenated phosphate esters	$\left(\text{Br} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array} \text{O} \right)_3\text{—PO}$
Halogenated phosphonate esters	$(\text{CH}_3\text{CH}_2\text{O})_2\text{—}\overset{\text{O}}{\parallel}\text{P}\text{—CH}_2\text{CH}_2\text{Br}$
Halogenated hydrocarbons	Chlorinated paraffins $\text{—}(\text{CH}_2)_x\text{—}(\underset{\text{Cl}}{\text{CH}})_y\text{—}$
<b>Nonreactive, inorganic</b>	
Antimony oxide	$\text{Sb}_2\text{O}_3$
Aluminum oxide trihydrate	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Zinc borate	$\text{Zn}_2\text{B}_6\text{O}_{11}$
Ammonium orthophosphate	$(\text{NH}_4)_3\text{PO}_4$
Ammonium sulfamate	$\text{NH}_4\text{SO}_3\text{NH}_2$
<b>Reactive</b>	
Bromine and/or phosphorus-containing polyols	$\begin{array}{c} \text{CH}_2\text{OOCR} \\   \\ \text{CHOOCR} \\   \\ \text{CH}_2\text{OOCR} \end{array} \quad \text{R} = \begin{array}{c} \text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{—CH}(\text{Br})\text{—CH}(\text{Br})\text{—}(\text{CH}_2)\text{—} \end{array}$
Halogenated phenols	
Tetrachlorophthalic anhydride	
Phosphonate esters	$\text{H}(\text{OCH}_2\text{CH}_2)_x\text{O}_2\text{—}\overset{\text{O}}{\parallel}\text{P}\text{—CH}_2\text{OH}$
Dibromoneopentyl alcohol	$(\text{BrCH}_2)_2\text{—C}(\text{CH}_2\text{OH})_2$

**Table 2. Typical flame retardants used in finishes.**

	Structure	Reference
Tetrakis(hydroxymethyl)phosphonium chloride (THPC)	$\left[ \begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{HOCH}_2-\text{P}-\text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array} \right]^{\oplus} \text{Cl}^{\ominus}$	(4-7)
THPC-NaOH-NaCl		(8, 9)
N-Methylol dimethylphosphonopropionamide	$(\text{CH}_3\text{O})_2-\overset{\text{O}}{\parallel}{\text{P}}-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHCH}_2\text{OH}$	(10, 11)
Cyanamide-phosphoric acid	$\text{H}_2\text{NCN} + \text{H}_3\text{PO}_4$	(12)
Tris(2,3-dibromopropyl) phosphate	$(\text{CH}_2-\underset{\text{Br}}{\underset{ }{\text{CH}}}\text{CH}_2\text{O})_3 \text{PO}$	(13)

**Table 3. Typical flame retardants in coatings.**

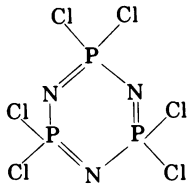
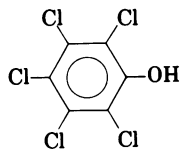
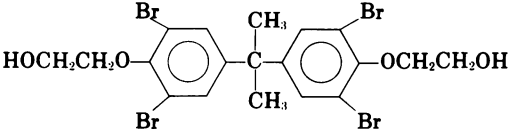
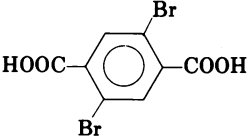
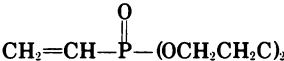
	Structure	Reference
Nonintumescent coatings		
Phosphonitrilic chloride in urethane coatings		(14)
Chlorinated aromatics and aliphatics (with and without antimony oxide)		(15, 16)
Chlorinated paraffins (70% Cl)		
Zinc borate in resin formulations		(17, 18)
Intumescent coatings		
Halogenated alkyl phosphates in resins	$(\text{CH}_2-\underset{\text{Br}}{\underset{ }{\text{CH}}}\text{CH}_2\text{O})_3 \text{PO}$	(19)
Ammonium polyphosphate in resins	$\text{NH}_4\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{O})_2-\text{NH}_4$	(20)
Boric acid or borax or zinc borate in resins	$\text{H}_3\text{BO}_3; \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ $3\text{ZnO} \cdot 2\text{B}_2\text{O}_3$	(21, 22)

Table 4. Typical flame retardants used as monomers in copolymerization or grafting.


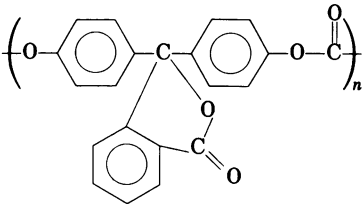
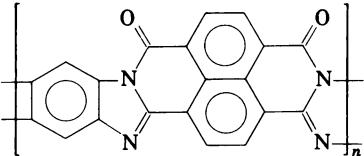
	Structure	Reference
Vinyl chloride or bromide	$\text{CH}_2=\text{CHCl}$ , Br	(23)
Vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	(24)
2,2-Bis[3,5-dibromo-4-(2-hydroxyethoxy)phenyl]propane		(25)
2,5-Dibromoterephthalic acid		(26)
Bis(2-chloroethyl) vinyl phosphonate		(27)

ing four ways: (1) by using flame retardants as additives prior to polymer processing; (2) by using them as a finish or a surface coating; (3) by using flame retardants as comonomers in the polymerization or grafting; (4) by synthesizing inherently flame resistant structures.

The flame retardants used as additives can be subdivided into nonreactive and reactive types, and the nonreactive type can be further divided into organic and inorganic additives. Although a very large number of flame retardants can be used as additives, at this time a small group of distinct chemical types dominates the field. Table 1 illustrates typical examples of these (2,3).

Table 2 lists the more popular flame retardants used in textile finishes (4-13). Typically, the finishing formations include one or more of such other components: urea, a triazine resin, methylol melamine, ammonia, or a halogenated alkyl phosphate. Flame retardant coatings are of two types: those that are merely flame-resistant and those that are also intumescent. When heat is applied to such a coating, combustion produces a residue which is puffed up by the escaping gases and the resulting cellular material (foam) may actually insulate and protect a flammable substrate. Table 3 illustrates examples of both types (14-22). Table 4 illustrates some of the more commonly used flame retardants as monomers in copolymerization or grafting (23-27).

Table 5. Polymeric structures with inherently high flame resistance.

	Structure	Reference
<i>p</i> -Polyphenylene		(31, 32)
Phenolphthalein polycarbonate		(28)
Oxobenz[de]imidazobenzimidazoisoquinoline (benzimidazobenzophenanthroline-type ladder polymer, BBL)		(33)

A number of studies on new high-temperature polymers have correlated the structure of polymers with their flame resistance properties (28-30). One general conclusion can be drawn—high flame resistance can be related to the

**Table 6. High temperature-resistant polymers.**

	Structure
Nomex	
Kynol	
PBI	

number of moles of multiple bonded aromatic rings per gram of polymer. Table 5 illustrates some examples of such polymeric structures (33). These are the current space-age products in research or development stages. However, as a result of the research efforts of private industry and the various government agencies, a new class of high temperature resistant polymers is available commercially as textiles and/or films. For example, Table 6 lists such names as Nomex, Kynol, and PBI (polybenzimidazole), which are associated with this class of materials. These are all materials containing high aromatic ring content and intrinsically improved flame retardance properties. They are presently expensive and will receive more importance as government-regulated markets require their use during the next decade.

## Typical Flame-Retarded Polymers

Because of the enormous amount of literature available on flame retardants and flame retarded polymers, only the most recent literature will be reviewed here. For example, in a recent book (34) more than 420 flame retardants were identified by their chemical structure

and more than 170 flame retardants were listed as proprietary. According to a 1972 directory (35), some 70 major manufacturers were producing flame retardants.

It is important to briefly review the major resin types and the quantities manufactured in the United States during 1973 (Table 7) (36). Polyethylene, polystyrene and styrene copolymers, poly(vinyl chloride) and copolymers, polypropylene, phenolics, urethane foam, polyesters, urea, and melamine constitute about 89% of all the resins manufactured, and the quantity produced of each of these is more than a billion pounds per year. Table 8 illustrates the pattern of consumption for these top eight resins (36). The pattern of consumption reveals that each type of resin is used in markets that require improved flame retardant properties. Table 9 illustrates typical flame retardants used in commercial plastics (37-53). Since polyethylene and polypropylene usually respond similarly to the same flame retardants, they are considered together. The most effective and and commonly used flame retardants for these polyolefins are combinations of antimony oxide and halo-organic compounds (54-57). Phosphorus-halogen flame retardant systems have been also increasingly found to be satisfactory for polyolefins (38,58). Effective flame retardant combinations for polystyrene and its copolymers are: halogen-containing compounds with or without antimony oxide, and halogen and phosphorus combinations with or without antimony oxide. Poly(vinyl chloride) and its copolymers contain an appreciable amount of halogen (56.8% in PVC). Thus, incorporation of antimony oxide gives an effective flame-retardant composition (42,59). Other very effective retardants are phosphorus-based systems which are used to balance off phthalate plasticizer effects (44). Phenolics are not especially flammable, mainly because of their high aromatic content. However, in some applications improvement in flame resistance is sought. Phosphorus and nitrogen compounds have been reported effective in improving flame resistance of phenolics (45). The use of chlorinated compounds (for example, chlorinated phenols) (60) as well as halogen- and phosphorus-containing compounds has been patented (46). The majority of polyurethane flame retardants are based on phosphorus. These may include phosphates and halogenated phosphates (61) as well as ammonium polyphosphate (47). Although halo-

gen and phosphorus compounds are used for polyesters individually, the combination of both is claimed to be more effective than either compound alone (50,62). Combinations of halogen compounds with antimony oxide are also important (51). The urea and melamine resins—apparently because of the high nitrogen content—are self-extinguishing. If these resins are cured in the presence of phosphoric acid, additional flame resistance is imparted (52). Tris(2, 3-dibromopropyl) phosphate has been also found to be an effective flame retardant for urea and melamine resins (53).

In summary, the commercially used flame retardants for the top eight classes of plastics are generally limited to the following types of compounds:

halogen; phosphorus; antimony oxide; halogen + antimony oxide; halogen + phosphorus; phosphorus + nitrogen.

Table 10 summarizes the types of commercially preferred flame retardants from the patent literature.

## Some Statistics on Flame Retardants

### Flame Retardant Markets

Flame retardant markets and their size (63) estimated for 1971 and projected for 1975 are illustrated in Table 11. The figures are all based on pre-energy-shortage data. Existing

Table 7. Resins manufactured during 1973.\*

Resin	Amt manufactured, lb
Polyethylene	8,619,600,000
Polystyrene and styrene copolymers	5,295,400,000
Poly(vinyl chloride) and copolymers	4,776,200,000
Polypropylene	2,151,600,000
Phenolics	1,438,800,000
Urethane foam	1,304,600,000
Polyester	1,091,200,000
Urea and melamine	1,020,800,000
Other vinyls	860,200,000
Alkyds	752,400,000
Acrylics	512,260,000
Coumarone-indene and petroleum resins	345,400,000
Epoxies	217,800,000
Nylons	176,000,000
Cellulosics	169,400,000
Others, (polyacetals, fluoroplastics, polycarbonates, silicones)	26,840,000
<b>TOTAL:</b>	<b>ca. 29,000,000,000</b>

\* Literature data (36).

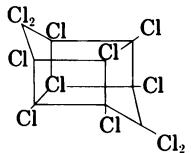





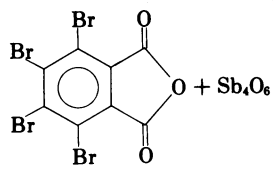

Table 8. Pattern of consumption of resins.\*

Resin and form or application	Consumption, lb
Polyethylene (high and low density)	
Film	3,273,600,000
Injection molding	1,249,600,000
Blow molding	1,060,400,000
Extrusion coating	519,200,000
Wire and cable	497,200,000
Pipe and conduit	334,400,000
Polyethylene film	
Trash bags, related products for home, industrial, institutional use	580,800,000
Miscellaneous packaging including miscellaneous food	407,000,000
Miscellaneous nonpackaging	275,000,000
Produce packaging	250,000,000
Industrial liners, shipping bags	226,600,000
Food and baked goods packaging	224,400,000
High density film	72,000,000
Non-packaging uses	1,237,800
Polystyrene and styrene copolymers (including ABS resins)	
Packaging	633,600,000
Paper and textile treating and coating	448,800,000
Toys	418,000,000
Housewares	411,400,000
Appliances	402,600,000
Poly(vinyl chloride) and copolymers	
Pipe and conduit	1,155,000,000
Flooring	464,200,000
Electrical wire and cable	426,800,000
Furniture	319,000,000
Upholstery and seat covers	182,600,000
Polypropylene	
Filament and fiber	660,000,000
Transportation including battery cases	308,000,000
Packaging film	143,000,000
Appliances	96,000,000
Phenolics	
Molding compounds	380,820,000
Plywood	275,000,000
Insulation material	246,400,000
Electrical and electronic switches, etc.	134,000,000
Urethane foam	
Furniture	369,600,000
Transportation	363,000,000
Building insulation	143,000,000
Bedding	114,400,000
Polyester	
Reinforced plastics other than sheet	605,000,000
Reinforced plastic sheet	237,600,000
Urea and melamine	
Bonding and adhesive resin for fibrous and granulated wood	576,400,000
Molding compounds	96,000,000
Adhesive for plywood	88,000,000

\* Literature data (36).

regulations make the carpets and rugs market the largest market for flame retardants. It is also one of the fastest growing markets because practically no flame retardants were used in this area as recently as 7–8 yr ago. Hydrated alumina, selling for under 10¢/lb, is the

Table 9. Typical flame retardants in commercial plastics.

Plastic	Flame retardant	Reference
Polyethylene, polypropylene	$\text{Sb}_4\text{O}_6 + [(\text{BrCH}_2)_3\text{CCH}_2]_2\text{O}$	(37)
	$[(\text{NCCCH}_2\text{CH}_2)_3-\text{P}^{\oplus}-\text{CH}_2\text{CH}_2-\text{P}^{\oplus}-(\text{CH}_2\text{CH}_2\text{CN})_3] 2\text{Br}^{\ominus} + \text{C}_6\text{Br}_6$	(38)
	$\text{NH}_4\text{BF}_4 + \text{Sb}_4\text{O}_6$	(39)
Styrene and styrene copolymers	$\text{Sb}_4\text{O}_6 + $  $; \text{PVC}$	(40)
	$(\text{CH}_2\text{CHCH}_2\text{O})_3\text{PO}$ 	(41)
Poly(vinyl chloride) and copolymers	$\text{Sb}_4\text{O}_6$	(42)
	$\text{Sb}_4\text{O}_6 - \text{CaCO}_3$	(43)
	$\text{R} \left( \text{C}_6\text{H}_4 - \text{O} \right)_3 \text{PO}$	(44)
Phenolics	$\text{POCl}_3 + \text{NH}_3$	(45)
	$\text{ClCH}_2\text{CH}_2\text{O}$  $\text{PO} + \text{chlorinated polyphenyl}$	(46)
	$(\text{Br}-\text{CH}_2\text{CH}_2\text{O})_2$	
Urethane foam	$(\text{NH}_4\text{PO}_3)_n$	(47)
	$(\text{CH}_2\text{CH}_2\text{O})_3-\text{PO}$ 	(48)
	$(\text{CH}_2\text{CHCH}_2\text{O})_3-\text{PO}$ 	(49)
Polyesters	$(\text{CH}_2\text{CHCH}_2\text{O})_3-\text{PO}$ 	(50)
	 $+ \text{Sb}_4\text{O}_6$	(51)
Urea and melamine resins	$\text{H}_3\text{PO}_4$	(52)
	$(\text{CH}_2-\text{CHCH}_2\text{O})_3-\text{PO}$ 	(53)



dominant flame retardant in this area. Transportation and home furnishings are two areas coming most recently under legislation and are consequently projected to have the most dramatic increase in usage of fire retardants. In general, the economic factor is a tremendous force in regulating the flame retardant market volume. The volume of all flame retardants with a price tag of more than 10¢/lb is only 1/3 of the total market volume.

### Flame Retardant Growth in Plastics

Table 12 illustrates the increasing utilization of flame retardants (more than 41% growth between 1972 and 1973) in commercial plastics (64). The items of special note in the nonreactive flame retardant areas are that there has been more than a 60% increase in use of halogenated phosphate esters, and more than 80% increase in various other types of nonreactive flame retardants. Thus, the trend is towards phosphorus-halogen and numerous other specialized flame retardant systems. The overall reactive flame retardant growth was comparable to that of nonreactives, with the greatest increase occurring in the polycarbonate (80%) and epoxy (58%) resin systems. These, however, are low volume resins.

### Price Ranges of Common Flame Retardants

Table 13 lists some common types of flame retardants with their corresponding pre-energy-shortage price data (65). The cost can range from a few cents a pound to many dollars a

Table 11. Flame retardant markets.\*

Market	Estimated annual consumption, lb $\times 10^{-6}$	
	1971	1975
Carpets and rugs	100-125	425-550
Construction	14-22	75-100
Miscellaneous nondurables	10-15	15-20
Electrical and electronics	11-12	35-40
Apparel	8-10	34-36
Transportation	4-5	70-80
Home furnishings	3-4	20-25

\* Industry data (63).

Table 12. Flame retardant growth in plastics.\*

	Utilization of flame retardants, lb	
	1972	1973
<b>Nonreactive</b>		
Phosphate esters (non-halogenated)	53,680,000	74,140,000
Chlorinated paraffins	41,800,000	59,180,000
Phosphate esters (halogenated)	14,960,000	23,980,000
Antimony oxide	17,600,000	18,920,000
Bromine compounds	7,040,000	11,000,000
Boron compounds	3,960,000	4,840,000
Others	10,120,000	18,260,000
<b>Reactive</b>		
Urethane intermediates	18,040,000	23,100,000
Polyester intermediates	11,440,000	14,960,000
Epoxy intermediates	5,280,000	8,360,000
Polystyrene intermediates	—	2,200,000
Polycarbonate intermediates	1,100,000	1,980,000
Others	7,260,000	10,780,000

\* Industry data (64).

Table 10. Typical plastic-flame retardant combinations.

Plastic	Flame retardant*
Polyethylene	Sb <sub>2</sub> O <sub>3</sub> + X; P + X
Polypropylene	
Polystyrene	X $\pm$ Sb <sub>2</sub> O <sub>3</sub> ; P + X $\pm$ Sb <sub>2</sub> O <sub>3</sub>
Poly(vinyl chloride)	Sb <sub>2</sub> O <sub>3</sub> ; P
Phenolics	P + N; X; X + P
Polyurethane foam	P; P + X; P + N
Polyesters	X; P; X + P; X + Sb <sub>2</sub> O <sub>3</sub>
Urea and melamine	P; X + P

\* X = halogen-containing organic compounds; P = phosphorus-containing compounds; P + X = phosphorus- and halogen-containing organic compounds; P + N = phosphorus- and nitrogen-containing organic compounds; X + Sb<sub>2</sub>O<sub>3</sub> = halogen-containing compound combined with antimony oxide;  $\pm$  = composition with or without the following component.

pound for some flame and smoke retardants. The cost of the flame retardant may therefore rule out a plastic entirely from a certain application. On the other hand, a high concentration of low-cost flame retardant, such as hydrated alumina, may make the flame retarded formulation less expensive than the standard polymer formulation. Correspondingly, flame retardants with a price tag of less than 10¢/lb have captured about two-thirds of the total flame retardant market volume, and those with a price tag of more than 75¢/lb only a very small fraction (about 1%). It can be seen that the nondurable inorganic flame retardants constitute exclusively the lowest price (<10¢/lb) group of additives. The reactive flame retardants or those that are of most interest in

**Table 13. Price ranges for common flame retardants.\***

Product price range, (\$/lb)	Typical product
<10	Borax/borates Hydrated alumina Diammonium phosphate
10-25	Urea phosphate Other phosphates
25-50	Phosphate esters Chlorinated hydrocarbons
50-75	Halogenated phosphates Antimony oxide
>75	Phosphine derivatives

\* Data for 1973 (65).

plastics and textile applications are those in the 25-50¢/lb and above range.

## Conclusions

The involvement by government agencies, consumer groups, and industry in safety programs during the 1970's will continue. Interest in increasing the fire safety aspects of polymers will grow, leading to the use of a number of fire retardant chemical approaches. These chemical approaches will utilize large quantities of halogen, antimony, phosphorus, nitrogen, and other inorganic, and aliphatic and aromatic organic species which will be added as non-reacted or reacted components of the polymer structure.

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